

EMULSION POLYMERISATION OF STYRENE IN A CONTINUOUS STIRRED TANK REACTOR

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By

DHRUBO BHATTACHARYA

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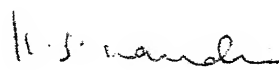
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CERTIFICATE

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This is to certify that the present work 'EMULSION
POLYMERISATION OF STYRENE IN A CONTINUOUS STIRRED TANK
REACTOR' has been carried out under my supervision and
has not been submitted elsewhere for a degree.

Date: 6th December 1980


[K.S. Gandhi]
Professor
Department of Chemical Engineering
Indian Institute of Technology
Kanpur-208016, India

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ABSTRACT

Thompson and ^{Co-workers} ~~Stevens~~ [13] proposed a model for emulsion polymerisation in a C.S.T.F., based on the population balance approach and instantaneous termination of radicals. Their model has been extended by integrating the work of Sundberg [17] and Min [22] to calculate the molecular weight distribution, total number of particles, rate of polymerisation and the absolute particle size distribution. Chain transfer to monomer has also been included in the model. Effect of process variables viz; i) Initiator concentration, ii) Soap and iii) Residence time on these quantities has been studied. The theoretical predictions have been found to be similar to those of DeGraff's [20] and in some cases are better than the latter. Some experiments on the emulsion polymerisation of styrene in a C.S.T.F. have been done. These experimental results do not compare well with the theoretical predictions because of some inadequacies of the apparatus.

CHAPTER 1

INTRODUCTION

Tracing the history of emulsion polymerisation process, one finds that it dates back to about fifty years. It has gained great popularity in industry and has been to-date one of the most important processes for the manufacture of rubbers, plastics, coatings and finishes..

The factors which have contributed to emulsion polymerisation's utility are i) easy operation of the reactor ii) good temperature control iii) low viscosity of polymer latex, and iv) considerably higher molecular weights, at high reaction rates than that obtained by bulk techniques.

The commercial techniques can be broadly classified into i) batch and ii) continuous systems. The batch system employs simple equipment and is extensively used for low production rates and specialty applications.

Batch processes have been exhaustively studied by Harkins [1], Smith and Ewart [2] and Gardon [3] etc. The major theoretical and experimental aspects have been reviewed by Alexander and Naper [4] , Vander Hoff [5] and Min and Ray [6] .

The increasing demand of polymers has necessitated the use of continuous reactors and much attention has been given to their study. The scientific understanding of the continuous process is still far from complete as it involves some conceptual problems that are absent in batch systems. For example, one such point of interest is the stability of continuous emulsion reactors. Gershberg and Longfield [7] noted periodic behavior under steady inputs in their early experiments. Similarly Omi et al. [8] observed oscillatory behavior when polymerising styrene in emulsion. Satisfactory modelling of this behavior is yet to be done. Yet another problem is to find the equivalents of reaction regimes 1, 2 and 3 of batch systems, since in a well stirred system, micelles and monomer droplets can never disappear.

In a continuous stirred system the various species spend unequal times in the reactor. The concept of residence time distribution of the particles has been exploited by some workers. These investigators theorised that each particle is a small independent batch reaction unit and resides for different times in the reactor. A knowledge of batch behavior combined with the RTD is assumed to represent the C.S.T.R. characteristics. The major difficulties with this approach are i) complex and long computations and ii) the difficulty of identifying the regime to be used for formulation.

Hulburt and Katz's work [9] has generated interest in the application of the population balance technique to emulsion polymerisation. Funderbunk [10] and Stevens and Funderbunk [11] illustrated the use of population balances in a C.S.T.R. These workers were followed by Thompson [13], Stevens [12], Cauley and Giglio [13]. Their work will be reviewed in detail in the next chapter.

Min and Ray proposed the most comprehensive population balance model taking into account a variety of physical effects but, did not generate numerical results [14]. Ballal [15] used Min and Ray's model for his work. He could obtain number of particles, particle size distribution, rate of polymerisation and the molecular weight distribution but his model was too complicated and his calculations were time consuming.

The present work has been done using Thompson and Stevens model [12] which is much simpler than Min and Ray's [14]. This model has been suitably modified to generate molecular weight distribution, rate of polymerisation, the total number of particles and particle size distribution. A variety of physical effects have been accounted for. The theoretical predictions have been compared with the experimental data of DeGraff and Pohlein [16].

Some experiments have been conducted on a C.S.T.R. using styrene as monomer, Potassium persulfate as initiator and Potassium oleate as the emulsifier.

CHAPTER 2

PHYSICAL PROCESSES AND MODEL

The constituents of the emulsion are i) water, ii) monomer, iii) soap and iv) initiator. Water forms the continuous phase. Monomer is generally insoluble in water. It is present mainly in the form of drops and to a minor extent in the dissolved state. Monomer also gets 'solubilised' in the soap micelles. The soap forms micelles and some goes to stabilise monomer drops and polymer particles. A negligibly small amount goes into solution. The initiator chosen is water soluble and thermally dissociates into radicals.

Some of the initiator radicals are captured by micelles and polymerisation is initiated. Thus polymer particles are created. Poe [18] proposed that the initiator may polymerise the dissolved monomer in the aqueous phase. Such radicals may interact to produce dead chains, which might precipitate. Such dead chains may coagulate and also form particles. The live radicals created in the polymer particles may desorb. Some workers proposed that live radicals desorbing from particles may react with radicals in the aqueous phase to precipitate dead chains. And as mentioned earlier these dead chains on coagulation may nucleate particles.

The initiator radicals can also enter polymer particles and generate growing polymer radicals. They can also terminate existing live radicals in particles. Yet another phenomenon is the desorption of live radicals. Some workers have proposed that desorbed live radicals may re-enter the polymer particles. Due to the variety of physical processes there can be different number of radicals in different particles. Live radicals grow for different times. This generates a distribution in molecular weights.

The monomer concentration in particles is maintained constant by diffusion from the monomer droplets while polymerisation proceeds in the polymer particles. The live radicals can transfer their activity by reacting with a chain transfer agent or monomer to create a dead chain and a live radical. Due to the growth of live radicals within the polymer particles, the latter grow in size. Since particles form at different times and grow intermittently there is a particle size distribution.

The monomer droplets and polymer particles are stabilised by adhering soap. (In spite of this there may be coagulation of the polymer particles). The micelles break up to provide the soap required for stabilising the growing particles.

A model then has to account for all these processes to predict the particle size distribution, number of particles, rate of polymerisation and molecular weight distribution. All these processes have been incorporated in Min and Ray's [14] population balance model. But they did not give numerical results. Most workers have generally neglected the following processes: i) particle coalescence, ii) chain transfer, iii) initiation in the aqueous phase, iv) particle formation by precipitation of dead chains and coagulation in the aqueous phase and v) re-entry of live radicals into particles.

Funderbunk [10] and Funderbunk and Stevens [11] wrote population balances for a C.S.T.R. They calculated only the particle size distribution. They did not consider live radical desorption. They assumed that all particles contain the same number of radicals. They assumed the value to be that given by Stockmayer [19] which required the evaluation of an integral of a complicated ratio of Bessel functions.

Thompson and Stevens [12] combined particle size variation with the Smith-Ewart [2] recursion relation for radical balance in their population balance model. Gardon's [3] expression for particle growth rate was used and was assumed to be independant of particle size. A feed stream free of

polymer particles was assumed. Radical capture was assumed to be proportional to the exposed surface area of the particles and micelles. They calculated the dimensionless number density of the particles as a function of their size. However the total number of particles, the rate of polymerisation and the M.W.D. of the polymer product were not calculated.

Thompson et al. [13] used the model of Thompson and Stevens [12] (TS Model). They assumed instantaneous termination of live radicals in particles. This implies the presence of either zero or one radical in the polymer particle. They could obtain analytical solution of the two population balance equations framed for the two types of particles. They calculated the non-dimensional particle size distribution and compared these with Funderbunk's experimental data [10,11]. However the criticism levelled against Thompson and Stevens work remains valid here too. The absolute value of the total number of particles could not be calculated since the variables in the balance equations were made dimensionless using NT_0 , the number of zero-size micelles, which could not be estimated. For the same reason rate of polymerisation could not be calculated.

It is to be noted that T.S. model is incapable of computing M.W.D.

Recently Sundberg [17] in his batch study of emulsion polymerisation used population balances. He made variables dimensionless by choosing measurable quantities. Alongwith the population balances he wrote a material balance on soap and solved a set of simultaneous partial integro-differential equations numerically to obtain the absolute particle size distribution. He also obtained the polymerisation rate and conversion as a function of time. Radical desorption was not considered in his model.

The present model combines the T.S. model with Sundberg's model and Min's [22]work for the study of emulsion polymerisation in a C.S.T.R. Particle size distribution, number of particles, rate of polymerisation and M.W.D. have been calculated.

CHAPTER 3

MODELLING EQUATIONS

The following assumptions have been made in this chapter:-

(i) It has been assumed that as soon as a primary radical enters the polymer particle, instantaneous termination of growing radicals occurs. This implies that only two types of particles are present in the emulsion; a) particles which contain one live radical and b) particles which do not contain any radical. Radicals and dead chains can be of various length and are housed in the particles.

(ii) The micelles and polymer particles are presumed to be the sole sites for all reactions except for the dissociation of initiator molecules. Capture of initiator radicals is assumed to be proportional to the surface area of micelles and polymer particles.

(iii) The reactor feed is assumed to be free of polymer particles.

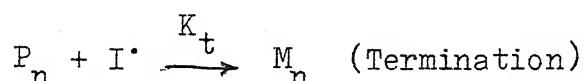
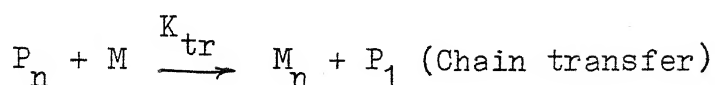
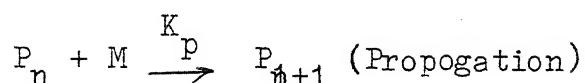
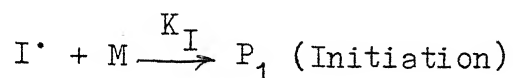
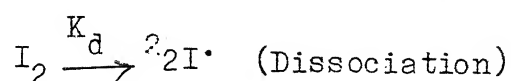
(iv) Particle growth rate is assumed to be independent of particle size. Gardon's expression; $\frac{dv}{dt} = Ki$ is used where K is the growth rate of a particle containing a single radical, i is the number of radicals per

particle and v is the volume of the particle.

(v) The initiator radical has been treated as a polymer radical of unit length.

(vi) All radicals in the particle are assumed to react with equal reactivity independent of their length.

The following kinetic scheme has been adopted:-



Population Balance Equations For Determining Size Distribution, N_T and R_p

Let $f(i,v)dv$ be the number of particles containing i radicals lying in the volume range of v to $v+dv$ per cc. of emulsion. Note that $i = 0$ or 1 only, since instantaneous termination has been assumed. Note that $f(0,v_m)$ does not denote micelles.

Following Thompson and Stevens [12] the population balance equations can be written as:-

$$\frac{\partial}{\partial v} \left[\frac{dv}{dt} \times f(0,v) \right] = 0 = R_{ia} a_p N_A [f(1,v) - f(0,v)] \\ + \frac{k_0 a_p}{v} f(1,v) - \frac{f(0,v)}{\tau}$$

L.H.S. is zero because $\frac{dv}{dt}$ is zero for particles which do not contain any radical. The first term on R.H.S. represents a gain and a loss term through radical capture. The second term represents a gain through desorption of live radical and the last term shows loss through outflow. Using dimensionless variables and parameters defined at the end of the chapter, we have:-

$$X_0 = (A_6 y^{-1/3} + A_4 y^{2/3}) \frac{X_1}{A_4 y^{2/3} + A_5} \quad (1)$$

Similarly

$$\frac{\partial}{\partial v} [Kf(1,v)] = R_{ia} a_p N_A [f(0,v) - f(1,v)] \\ - \frac{K_0 a_p}{v} f(1,v) - \frac{f(1,v)}{\tau}$$

Non-dimensionalising:-

$$\frac{dX_1}{dy} = A_4 y^{2/3} (X_0 - X_1) - \frac{A_6 X_1}{y^{1/3}} - A_5 X_1 \quad (2)$$

Adding (1) and (2):-

$$\frac{dX_1}{dy} = -A_5(X_0 + X_1) \quad (3)$$

Solution of this equation yields;

$$\begin{aligned} \ln \frac{X_1(y)}{X_1(1)} = & 2 A_5(1-y) - \frac{3 A_5}{A_4} (1-y^{1/3}) - \frac{3xA_6A_5}{2 A_4} \ln \frac{1+A_3y^{2/3}}{1+A_3} \\ & - \frac{3A_5}{A_3^{3/2}} [\tan^{-1}(A_3^{1/2} y^{1/3}) - \tan^{-1}(A_3^{1/2})] \quad (4) \end{aligned}$$

where $A_3 = A_4/A_5$

A b.c. has to be written to find $X_1(1)$. For this, the procedure given by Sundberg [17] is followed. Writing a balance in a volume of width ϵv_m (where ϵ is a small number), we have:-

$$\begin{aligned} K f(1, v_m + \epsilon v_m) = & R_{ia} a_p N_A \left[f(0, v_m + \frac{\epsilon v_m}{2}) - f(1, v_m + \frac{\epsilon v_m}{2}) \right] \epsilon v_m \\ & - \frac{K_o a_p}{v} f(1, v_m + \frac{\epsilon v_m}{2}) \epsilon v_m - \frac{f(1, v_m + \frac{\epsilon v_m}{2}) \epsilon v_m}{\tau} + R_{ia} m a_m N_A \quad (5) \end{aligned}$$

The growth rate terms have been written for particles coming in and leaving a volume element of ϵv_m at v_m and $v_m + \epsilon v_m$. The first, second and third terms have to be written for all particles lying in the volume range of v_m to $v_m + \epsilon v_m$. Hence their volume has been taken as the mean value in this

range, i.e. $v_m \neq \varepsilon v_m + \frac{m}{2}$. Here only one growth term (output) is present as a particle of volume v_m can not exist. The last term appears because of creation of particles from micelles at volume v_m .

Taking limit as $\varepsilon v_m \rightarrow 0$

$$K_f(1, v_m) = P_{ie} m a_m N_A$$

$$\text{or } X_1(1) = A_4 \frac{m}{m_0} \quad (6)$$

Material Balance For Soap: In a well stirred C.S.T.R., the concentration of species in the reactor is the same as the concentration of the species in the effluent stream. The polymerisation rate is proportional to the concentration of X_1 -type of particles (see eq.13). The concentration of X_1 -type of particles is proportional to m (from 6). Hence m , the number of micelles in the out flowing stream can never be zero, for the model to predict non-zero reaction rates. As long as the micelles are present, the soap concentration in the aqueous phase will be equal to the saturation concentration in water. Hence a material balance on soap would mean equating the soap supplied through micelles to the reactor, to the soap leaving the reactor in the form of soap on particle surface and monomer droplets, and, the free micelles in the output stream.

$$\therefore m_o a_m = m a_m + A_p + m_d v_d^{2/3} \frac{2/3}{3} (4\pi)^{1/3} \quad (7)$$

Monomer droplets though larger in size than micelles, are far fewer in number. Thus soap required to stabilize them may be neglected.

$$\text{or } m_o a_m = m a_m + \int_{v_m}^{\infty} f(o,v) a_p dv + \int_{v_m}^{\infty} f(1,v) a_p dv$$

on simplifying;

$$1 = \frac{m}{m_o} + \int_1^{\infty} X_o y^{2/3} dy + \int_1^{\infty} X_1 y^{2/3} dy \quad (8)$$

From (3) we have:

$$(X_o + X_1) y^{2/3} dy = -\frac{1}{A_5} \int_1^{\infty} \frac{dX_1}{dy} y^{2/3} dy$$

Simplifying after using $X_1(\infty) = 0$,

$$\frac{m}{m_o} = \frac{1}{1 + \frac{A_4}{A_5} + \frac{2A_4}{3A_5} \int_1^{\infty} \frac{X_1(y)}{X_1(1)} y^{-1/3} dy} \quad (9)$$

Substituting for $\frac{X_1}{X_1(1)}$ from (4), $\frac{m}{m_o}$ can be calculated.

$$\begin{aligned} \text{Now } N_T &= \int_{v_m}^{\infty} [f(o,v) + f(1,v)] dv \\ &= m_o \int_1^{\infty} (X_o + X_1) dy \end{aligned} \quad (10)$$

$$\text{From (3); } N_T = -\frac{m_o}{A_5} \int_1^{\infty} \frac{dX_1}{dy} dy$$

$$\text{Using (6), we have; } N_T = \frac{A_4}{A_5} \times \frac{m}{m_o} \times m_o \quad (11)$$

Thus N_T can be calculated.

Rate of polymerisation, R_p is given by:-

$$R_p = \frac{K_p (M_p) \times \text{radical conc.}}{N_A}$$

But radical concentration is given by the total number of particles containing one live radical/cc. of emulsion.

$$\therefore R_p = \frac{K_p (M_p)}{N_A} \times \int_{v_m}^{\infty} f(1, v) dv \quad (12)$$

$$= \frac{K_p (M_p)}{N_A} \times \frac{A_4 m}{m_0} \times m_0 \int_1^{\infty} \frac{X_1}{X_1(1)} dy \quad (13)$$

Therefore R_p can also be computed.

Particle size distribution can be obtained as follows:-

The cumulative size distribution is given by

$$F(y) = \frac{\int_{v_m}^y [f(0, v) + f(1, v)] dv}{\int_{v_m}^{\infty} [f(0, v) + f(1, v)] dv} \quad (14)$$

Using (3) and simplifying;

$$F(y) = 1 - \frac{X_1(y)}{X_1(1)} \quad (15)$$

Thus particle size distribution can be obtained.

Population Balance For MWD Determination

Let $L(n, v)dv$ be the number of particles lying in the volume range of v to $v+dv$, having a radical of length n .

$$\begin{aligned}
\therefore \frac{\partial}{\partial v} [KL(n,v)] &= - R_{ia} a_p N_A L(n,v) - \frac{K_o a_p}{v} L(n,v) \\
&+ R_{ia} a_p N_A f(0,v) \delta_{n1} + K_p(M_p) [L(n-1,v) - L(n,v)] \\
&- \frac{L(n,v)}{\tau} - K_{tr}(M_p) L(n,v) + K_{tr}(M_p) f(1,v) \delta_{n1} \quad (16)
\end{aligned}$$

The fourth term on R.H.S. represents a gain and a loss term through propagation. The last two terms have been written to account for chain transfer to monomer.

Non-dimensionalising (16), we have:-

$$\begin{aligned}
\frac{d}{dy} L^*(n,y) &= - A_4 y^{2/3} L^* - A_6 y^{-1/3} L^* + A_4 y^{2/3} X_o \delta_{n1} \\
&+ A_7 [L^*(n-1,y) - L^*] - A_5 L^* - A_8 L^* + A_8 X_1 \delta_{n1} \quad (17)
\end{aligned}$$

Following a similar approach as in (5) and writing of balance on a volume range of v_m to $v_m + \varepsilon v_m$ for $L(n,v)$;

$$\begin{aligned}
0 &= \dot{Q}L(n, v_m + \frac{\varepsilon v_m}{2}) \frac{\varepsilon v_m}{2} + KL(n, v_m + \frac{\varepsilon v_m}{2}) \cdot V_R \\
&- V_R f(0, v_m + \frac{\varepsilon v_m}{2}) \frac{\varepsilon v_m}{2} R_{ia} a_p N_A \delta_{n1} - V_R R_{ia} N_A a_m \delta_{n1} \\
&- K_{tr}(M_p) L(n, v_m + \frac{\varepsilon v_m}{2}) \frac{\varepsilon v_m}{2} \cdot V_R + K_{tr}(M_p) f(1, v_m + \frac{\varepsilon v_m}{2}) \times \\
&\varepsilon v_m \cdot V_R \delta_{n1} + V_R L(n, v_m + \frac{\varepsilon v_m}{2}) \cdot \frac{\varepsilon v_m}{2} \left(\frac{K_o a_p}{v} + R_{ia} a_p N_A \right) \quad (18)
\end{aligned}$$

L.H.S. is zero because there are no live radicals in the feed and $L(n, v_m)$ is zero for the same reason given for $f(1, v_m)$.

Taking limit as $\varepsilon v_m \rightarrow 0$

$$K L(n, v_m) = R_{ia} m a_m N_A \delta_{n1}$$

or $K L(n, v_m) = K f(1, v_m) \delta_{n1}$

$$\therefore L(1, v_m) = f(1, v_m)$$

and $L(n, v_m) = 0$ for $n > 1$

$$\therefore L^*(1, 1) = X_1(1) \quad (19)$$

Let $G_i(n, v)dv$ be the number of dead polymer chains of length n in particles containing i radicals and lying in the volume range of v to $v + dv$. Minimum value of n for $G_1(n, v)$ is 1 (obtained by the chain transfer to monomer by an initiator radical) and for $G_0(n, v)$ is 2 (obtained by termination of an initiator radical).

$$\begin{aligned} \therefore 0 = & - \frac{G_0(n, v)}{\tau} - G_0(n, v) R_{ia} a_p N_A + [L(n-1, v) \\ & + G_1(n, v)] R_{ia} a_p N_A + \frac{G_1(n, v) K_o a_p}{v} \end{aligned} \quad (20)$$

Non-dimensionalising (20);

$$0 = - A_5 G_o^* - A_4 y^{2/3} (G_o^* - G_1^*) + \frac{A_6 G_1^*}{y^{1/3}} + A_4 y^{2/3} L^*(n-1, y) \quad (21)$$

and ,

$$\begin{aligned} v \frac{\partial}{\partial v} [K G_1(n, v)] = & - \frac{G_1(n, v)}{\tau} + G_0(n, v) R_{ia} a_p N_A + K_{tr} \left(\frac{M_p}{M_p} \right) L \\ & - G_1 R_{ia} a_p N_A - \frac{G_1 K_o a_p}{v} \end{aligned} \quad (22)$$

Non-dimensionalising (22):-

$$\frac{dG_1^*}{dy} = -A_5 G_1^* + A_4 y^{2/3} (G_0^* - G_1^*) - \frac{A_6 G_1^*}{y^{1/3}} + A_8 L^*(n, y) \quad (23)$$

Writing a balance on $G_0(n, v)$ in the volume range of v_m to

$v_m + \varepsilon v_m$,

$$0 = G_0(n, v_m + \frac{\varepsilon v_m}{2}) \frac{\varepsilon v_m}{\tau} - R_{ia} a_p N_A [L(n-1, v_m + \frac{\varepsilon v_m}{2}) + G_1(n, v_m + \frac{\varepsilon v_m}{2})]$$

$$\varepsilon v_m + R_{ia} a_p N_A \varepsilon v_m G_0(n, v_m + \frac{\varepsilon v_m}{2}) - \frac{K_o a_p}{v} \varepsilon v_m G_1(n, v_m + \frac{\varepsilon v_m}{2})$$

$$\text{as } v_m \rightarrow 0$$

....(24)

The second term on R.H.S. represents a gain, first through radical capture by $L(n-1, v_m + \frac{\varepsilon v_m}{2})$, which creates a dead chain of length n and then by radical capture by $G_1(n, v_m + \frac{\varepsilon v_m}{2})$, which creates a G_0 type of chain of length n .

Taking limit of $\varepsilon v_m \rightarrow 0$

$$\frac{K_o a_m G_1(n, v_m)}{v} + R_{ia} a_m N_A [L(n-1, v_m) + G_1] = \frac{G_0(n, v_m)}{\tau} + R_{ia} a_m N_A G_0(n, v_m) \quad (25)$$

On taking a similar balance on $G_1(n, v)$ we have:-

$$0 = \frac{G_1(n, v_m + \frac{\varepsilon v_m}{2})}{\tau} \varepsilon v_m + K G_1(n, v_m + \frac{\varepsilon v_m}{2}) \frac{\varepsilon v_m}{v} - \frac{K_o a_p}{v} G_1(n, v_m + \frac{\varepsilon v_m}{2}) \varepsilon v_m + R_{ia} a_p N_A G_1(n, v_m + \frac{\varepsilon v_m}{2}) \varepsilon v_m - R_{ia} a_p N_A G_0(n, v_m + \frac{\varepsilon v_m}{2}) \varepsilon v_m + K_{tr}(M_p) L(n, v_m + \frac{\varepsilon v_m}{2}) \varepsilon v_m \quad \dots\dots\dots (26)$$

Taking limit, $\epsilon v_m \rightarrow 0$, we have:-

$$G_1(n, v_m) = 0 \text{ for any } n.$$

$$\text{Now from (25) :- } G_0(2, v_m) = \frac{R_{ia} a_m N_A f(1, v_m)}{\frac{1}{v} + R_{ia} a_m N_A}$$

$$\text{and } G_0(n, v_m) = 0 \text{ for } n > 2.$$

Solution of (21) and (23) would yield the values of G_0^* and G_1^* for various values of y . Hence a plot of

$\int_{v_m}^{\infty} n(G_0 + G_1) dv / \int_{v_m}^{\infty} n(G_0 + G_1) dv$ vs. n could be made, which would constitute the M.W.D. of the polymer product.

NOMENCLATURE

| | |
|---------------|--|
| a_m | surface area of each micelle, cm^2 |
| a_p | surface area of particle of size v , cm^2 |
| A_p | total surface area of particles, cm^2/cm^3 emulsion |
| d_p | density of polymer, gms/cm^3 |
| d_m | density of monomer, gms/cm^3 |
| i | number of radicals in a particle, dimensionless |
| (M_p) | concentration of monomer in the particles, moles/cm^3 |
| k_d | rate constant for dissociation of initiator in aqueous phase, $1/\text{cms}$ |
| k_p | rate constant for propagation, $\text{cm}^3/\text{mole}.\text{sec.}$ |
| k_o | rate constant for radical desorption, cms/sec |
| m | number of micelles, $1/\text{cm}^3$ emulsion, input |
| n | chain length of polymer, dimensionless |
| R_{ia} | rate of absorption of radicals in particles, and micelles, $\text{moles}/\text{sec}.\text{cm}^2$ |
| t | time, sec. |
| v | volume of particle, cm^3 |
| v_m | volume of micelle, cm^3 |
| v_d | volume of monomer droplets, cm^3 |
| V_R | volume of reactor, cm^3 |
| ϕ_m | monomer volume fraction in the particles, dimensionless |
| τ | mean residence time, sec. |
| δ_{ig} | Kronecker delta function, 1 for $i=g$, 0 for $i \neq g$ |

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| | |
|--------------|---|
| $f(i,v)dv$ | number of particles containing i radicals and lying in the volume range of v to $v+dv/\text{cm}^3$ emulsion |
| $L(n,v,)dv$ | number of particles containing a live radical of length n and lying in the volume range of v to $v+dv$ per cc. emulsion |
| $G_i(n,v)dv$ | number of dead chains of length lying in particles of volume ranging from v to $v+dv$ and containing i radicals/ cc. emulsion |
| K_{tr} | rate constant for chain transfer with monomer |
| S_i | moles of soap/cc. solution |
| a_s | surface area of soap per mole, cm^2/mole |
| m_o | number of micellse/cc. of inflowing solution |
| γ | $\frac{v}{V_m}$, dimensionless |
| N_A | Avagadro's Number |
| x_i | $f(i,v) \cdot V_m/m_o$ |
| L^* | $L \cdot V_m/m_o$ |

| | |
|---------|---|
| G_i^x | $G_i \cdot V_m/m_o$ |
| A_4 | $2 k_d [I]_i N_A^2 d_p (1 - \phi_m)^{5/3} \frac{2^{1/3}}{3} (4\pi)^{1/3} / (1 + K_d \tau) S_i a_s k_p d_m \phi_m$ |
| A_5 | $V_m/k\tau$ |
| A_6 | $K_o a_m (1 - \phi_m) d_p N_A / K_p \phi_m d_m$ |
| A_7 | $v_m N_A d_p (1 - \phi_m) / K_p M$ |
| A_8 | $K_{tr} V_m N_A d_p (1 - \phi_m) / K_p M$ |
| M | Mol. wt. of Styrene |

CHAPTER 4

METHOD OF SOLUTION

Determination of N_T and R_p

From (9), $m/m_{0.5}$ can be calculated once the integral in the denominator $\int_1^{\infty} X_1/X_1(1) \times y^{-1/3} dy$ has been evaluated.

For R_p , $\int_1^{\infty} X_1/X_1(1) dy$ has to be evaluated. Both these integrals were evaluated using a 5 point Legendre integration scheme, after converting the limits to the range of -1 to +1, using the following conversion:-

$$\int_a^b f(x)dx = \int_{-1}^{+1} f(n)dn \quad \text{where } n = \frac{2x-(a+b)}{b-a}$$

Here $a = 1$ and b was an arbitrarily chosen large number.

Convergence was tested by using different values of b till the value of the integral remained unchanged. See appendix II for the program used to integrate the expression.

Molecular Weight Determination

As it would be tedious to calculate all individual values of $L(n,v)$ and $G_1(n,v)$, Mink and Ray's procedure of using moments for generating M.W.D. has been followed here. The moments of the L distribution along with the moments of the $G_1(n,v)$ distribution has been used to generate the moments of M.W.D. These moments can then be used to generate the M.W.D.

Let \bar{L} be the z-transform of $L^*(n, y)$.

$$\therefore \bar{L} = \sum_{n=1}^{\infty} L^*(n, y) z^n$$

Multiplying (17) by z^n and summing from $n=1$ to ∞ we have,

$$\frac{d\bar{L}}{dy} = -\bar{L} (A_5 + A_8 + A_4 y^{2/3} + A_6 y^{-1/3}) + z(A_8 X_1 + A_4 X_0 y^{2/3} + A_7 \bar{L}) - A_7 \bar{L}$$

l_n , the n^{th} moment of $L^*(n, y)$, can be obtained from the z-transform, as follows:-

$$l_n = \left(z \frac{d}{dz} \right)^n \bar{L} \Big|_{z=1}$$

The differential equations for the moments of $L(n, v)$ distribution can then be written as:-

$$\frac{dl_n}{dy} = f l_n + {}^n C_0 l_0 A_7 + {}^n C_1 l_1 A_7 + {}^n C_2 A_7 l_2 + \dots + {}^n C_{n-1} A_7 l_{n-1} + g \quad \dots (29)$$

where $f = -(A_5 + A_8 + A_4 y^{2/3} + A_6 y^{-1/3})$ and $g = A_8 X_1 + A_4 X_0 y^{2/3}$

The b.c. for these equations are as follows:-

$$l_0 = l_1 = l_2 = l_3 = \dots = l_n = X_1(1), \text{ at } y = 1 \quad (30)$$

It is possible to obtain the moments of M.W.D. directly without computing the moments of $G_1(n, v)$.

Adding (21) and (23) we have:-

$$\frac{dG_1^*}{dy} = -A_5 (G_0^* + G_1^*) + A_4 y^{2/3} L^*(n-1, y) + A_8 L^*(n, y) \quad (31)$$

$$\text{Let } I_k = \int_1^x n^k (G_0^* + G_1^*) dy$$

Then I_k is proportional to the k^{th} moment of M.V.D.

$$\begin{aligned} \text{Then from (31):- } I_k &= \left\{ \sum_{n=0}^{\infty} \frac{n^k}{A_5} \left\{ -\frac{dG_1^*}{dy} + \left[A_4 y^{2/3} L^*(n-1, y) \right. \right. \right. \\ &\quad \left. \left. \left. + A_8 L^*(n, y) \right] \right\} dy \right. \end{aligned} \quad \dots(32)$$

We have seen that $G_1^*(1) = G_1^*(\infty) = 0$

$$\text{or } I_k = \int_1^{\infty} \sum_{n=0}^{\infty} \frac{n^k}{A_5} \left[A_4 y^{2/3} L^*(n-1, y) + A_8 L^*(n, y) \right] dy$$

$$\text{or } I_k = \frac{1}{A_5} \int_1^{\infty} A_4 y^{2/3} \sum_{n=0}^{\infty} (n+1)^k L^*(n, y) dy + \frac{A_8}{A_5} \int_1^{\infty} \sum_{n=0}^{\infty} n^k L^*(n, y) dy$$

$$\text{or } I_k = A_4/A_5 \int_1^{\infty} y^{2/3} \sum_{n=0}^{\infty} \sum_{p=0}^k \frac{k!}{p! (k-p)!} m^p L^*(m, y) dy + \frac{A_8}{A_5} \int_1^{\infty} l_k dy$$

Defining K_k as:-

$$K_k = \frac{A_4}{A_5} \int_1^x y^{2/3} \sum_{n=0}^{\infty} \sum_{p=0}^k \frac{k!}{p! (k-p)!} m^p L^*(m, y) dy + A_8/A_5 \int_1^x l_k dy$$

b.c.:- $K_k = 0$, at $X = 1$ and $K_k = I_k$
 $\lim_{x \rightarrow \infty}$

K_k on differentiating twice w.r.t. x yields a set of second order differential equations which can be solved using the equations (29) and (30). This would be a simpler method of obtaining I_k than by integrating (32).

$$\frac{dK_k}{dx} = \frac{A_4}{A_5} x^{2/3} \sum_{p=0}^k \frac{k!}{p! (k-p)!} l_p(x) + \frac{A_8}{A_5} l_k(x) \quad (33)$$

$$\therefore \frac{dk_0}{dx} = \frac{A_4}{A_5} x^{2/3} l_0(x) + \frac{A_8}{A_5} l_0(x) \quad (34)$$

$$\& \frac{d^2 K_0}{dx^2} = \frac{dK_0}{dx} \left[f + \frac{A_4}{(A_4 x^{2/3} + A_8)} x \frac{2}{3} x^{-1/3} \right] + g \left(\frac{A_4 x^{2/3} + A_8}{A_5} \right) \dots (35)$$

$$\frac{dK_1}{dx} = \frac{A_4}{A_5} x^{2/3} (l_0 + l_1) + \frac{A_8}{A_5} l_1 \quad (36)$$

$$\& \frac{d^2 K_1}{dx^2} = \frac{dK_1}{dx} \left(\frac{2}{3} x^{-1} - \frac{2}{3} x^{-1} x \frac{A_8}{A_4 x^{2/3} + A_8} + f \right) + \frac{dK_0}{dx} \frac{2}{3x} \frac{A_4 x^{2/3} A_8}{(A_4 x^{2/3} + A_8)^2} + C_0^1 + g \frac{2A_4 x^{2/3} + A_8}{A_5} \quad (37)$$

$$\text{where } C_0^1 = A_7$$

$$\frac{dK_2}{dx} = \frac{A_4}{A_5} x^{2/3} (l_0 + 2l_1 + l_2) + \frac{A_8}{A_5} l_2 \quad (38)$$

$$\& \frac{d^2 K_2}{dx^2} = \frac{dK_2}{dx} \left(f + \frac{2t}{3x} \right) + \frac{dK_1}{dx} \left(-\frac{4x^{1/3} t^2}{3} + C_1^2 + \frac{4tx^{-1/3}}{3} \right) + \frac{dK_0}{dx} \left(\frac{4xt^3}{3} - 2t^2 x^{1/3} + 2tx^{-1/3}/3 + 2tC_0^1 x^{2/3} - C_1^2 x^{2/3} t + C_0^2 \right) + \frac{g}{A_5} (A_8 + 4A_4 x^{2/3}) \dots \dots \dots (39)$$

$$\frac{dK_3}{dx} = \frac{A_4}{A_5} x^{2/3} (l_0 + 3l_1 + 3l_2 + l_3) + \frac{A_8}{A_5} l_3 \quad (40)$$

$$\begin{aligned}
& \& \frac{d^2 K_3}{dx^2} = \frac{dK_0}{dx} (3C_0^1 x^{2/3} t + 3C_0^2 x^{2/3} t + C_0^3 - C_2^3 t x^{2/3} \\
& + 2t^2 C_2^3 x^{4/3} - 3C_1^2 t^2 x^{4/3} - C_1^3 t^2 x^{2/3} + 4xt^3 + \frac{2x^{-1/3} t}{3} - 4t^2 x^{1/3} \\
& - 4x^{5/3} t^4 + 4xt^3 - \frac{2t^2 x^{1/3}}{3}) + \frac{dK_1}{dx} (C_1^3 + 4xt^3 - 6t^2 x^{1/3} + 2x^{-1/3} t \\
& - 2C_2^3 t x^{2/3} + 3C_1^2 x^{2/3} t) + \frac{dK_2}{dx} (C_2^3 + 2tx^{-1/3} - 2t^2 x^{1/3}) + \frac{dK_3}{dx} (f + \\
& \frac{2}{3} tx^{-1/3}) + (\frac{A_4}{A_5} t g + 7g \frac{A_4 x^{2/3}}{A_5}) \quad (41)
\end{aligned}$$

$$\begin{aligned}
\frac{dK_4}{dx} &= l_4 (\frac{A_8 + A_4 x^{2/3}}{A_5}) + 4l_3 \frac{A_4}{A_5} x^{2/3} + 6l_2 \frac{A_4}{A_5} x^{2/3} + 4l_1 \frac{A_4}{A_5} x^{2/3} \\
&+ \frac{A_4}{A_5} x^{2/3} l_0 \quad (42)
\end{aligned}$$

$$\begin{aligned}
& \& \frac{d^2 K_4}{dx^2} = l_4 (f \frac{A_4}{A_5} t + \frac{2}{3} \frac{A_4}{A_5} x^{-1/3}) + l_3 (4A_7 \frac{A_4}{A_5} t + 4 \frac{A_4}{A_5} f x^{2/3} \\
& + \frac{8}{3} x^{-1/3} \frac{A_4}{A_5}) + l_2 (\frac{6A_7 A_4}{A_5 t} + 12 \frac{A_4}{A_5} x^{2/3} A_7 + 4x^{-1/3} \frac{A_4}{A_5} \\
& + 6f \frac{A_4}{A_5} x^{2/3}) + l_1 (\frac{4A_7 A_4}{A_5 t} + \frac{12A_4 A_7}{A_5} x^{2/3} + \frac{12 A_4 A_7}{A_5} x^{2/3} \\
& + \frac{8}{3} x^{-1/3} \frac{A_4}{A_5} + \frac{4 A_4}{A_5} x^{2/3} f) + l_0 (\frac{A_7 A_4}{A_5 t} + \frac{4A_4 A_7}{A_5} x^{2/3} \\
& + \frac{6A_4 A_7}{A_5} x^{2/3} + \frac{4A_4}{A_5} x^{2/3} A_7 + \frac{A_4}{A_5} f x^{2/3} + \frac{2}{3} x^{-1/3} \frac{A_4}{A_5}) \\
& + \frac{g A_4}{A_5 t} + \frac{15A_4}{A_5} x^{2/3} g. \quad (43)
\end{aligned}$$

where

$$t = \frac{A_4}{A_4 x^{2/3} + A_8}, \quad C_0^2 = C_0^3 = A_7$$

$$C_1^2 = 2A_7, \quad C_2^3 = 3A_7 = C_1^3$$

The b.c. are as follows:-

$$\frac{dK_0}{dx} = \frac{A_4 + A_8}{A_5} X_1(1); \quad \text{when } x = 1$$

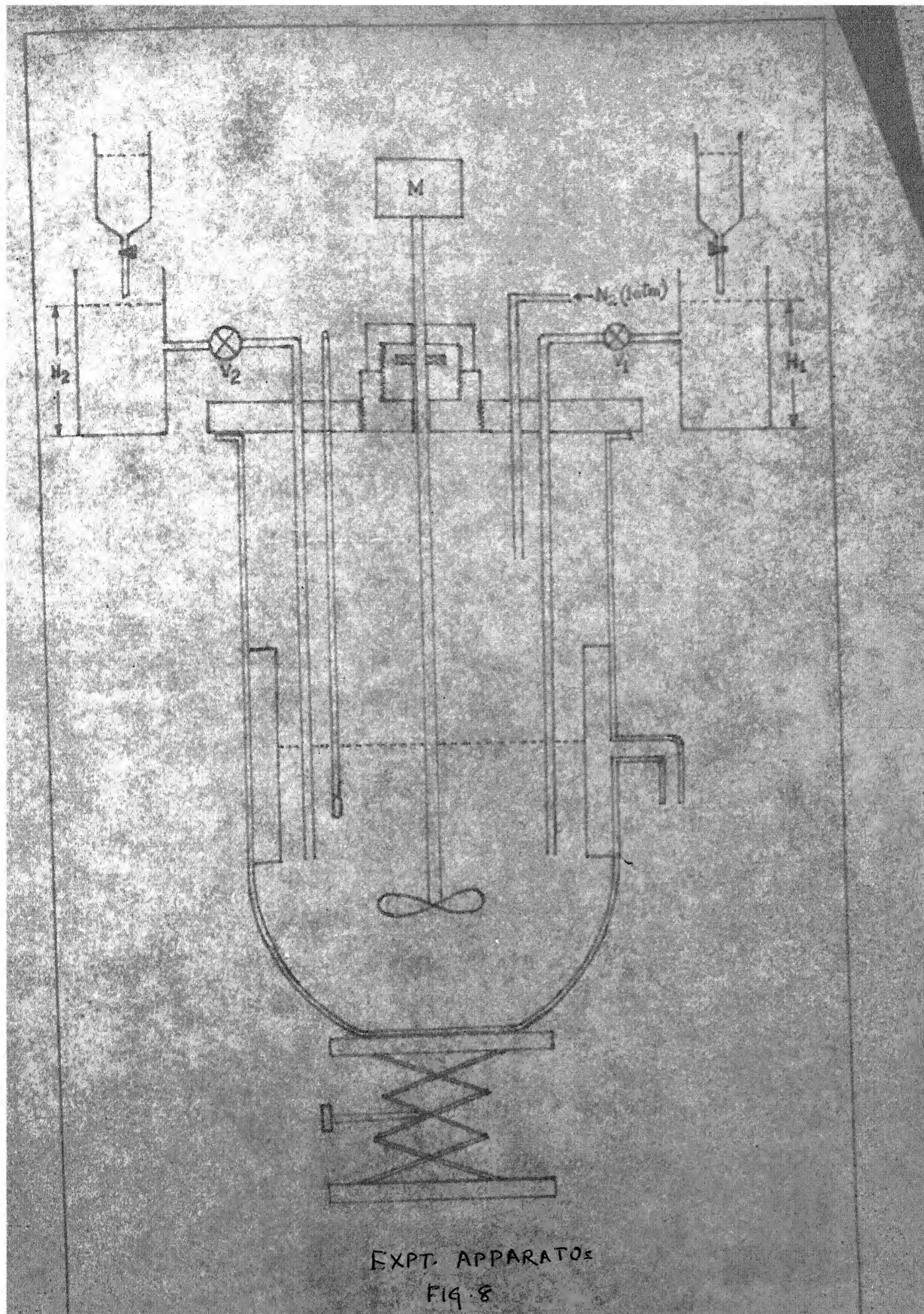
$$\frac{dK_1}{dx} = \frac{2A_4 + A_8}{A_5} A_4 \frac{m}{m_0} \quad \text{when } x = 1$$

$$\frac{dK_2}{dx} = \frac{4A_4 + A_8}{A_5} X_1(1) \quad \text{when } x = 1$$

$$\frac{dK_3}{dx} = \frac{8A_4 + A_8}{A_5} X_1(1) \quad \text{when } x = 1$$

$$\frac{dK_4}{dx} = \frac{16A_4 + A_8}{A_5} X_1(1) \quad \text{when } x = 1$$

Equations (34) to (43) have been solved by using a fourth order Gill's modified technique of Runge-Kutta method of numerical integration.



CHAPTER 5EXPERIMENTAL WORK

Apparatus:- A cylindrical glass vessel with a hemispherical bottom was used as the reactor. Three stainless steel baffles were used. The reactor had a side outlet which allowed a volume of 500 cc.s. of the emulsion to be present in the reactor at any time. A stainless steel lid rested closely on the flange of the vessel as shown in the figure 8. An adaptor was fitted centrally on it through which the stirrer rod was introduced. This was done to prevent leakage of the Nitrogen blanket and other vapors. A Remi stirrer (1/8 H.P.) was used to stir the reactor contents. Two stainless steel tubes passed vertically down through the lid and were used to feed the reactor with the monomer and soap solution respectively. The feed rates were adjusted using needle valves. The tubes were connected to two reservoirs filled with soap and monomer respectively. The levels of both in the reservoir were maintained to be constant manually. The reactor contents were heated by heating coil wrapped around the base of the reactor. The reactor rested on a screw jack so that it could be raised or lowered as desired to maintain proper head required for flow. The reactor contents were kept in an inert atmosphere by using nitrogen gas at one atmosphere pressure.

Experimental Procedure:

The styrene monomer was washed repeatedly using a 15% solution of KOH, to remove the inhibitor present in it. This was followed by washings with water to remove the last traces of KOH from the monomer. Next the required weight of the initiator (potassium persulfate) was dissolved in the soap (potassium oleate) solution.

The soap solution and the monomer were then allowed to flow into the reactor at the required flow rates. After some time, stirring was started. When the level of the emulsion in the reactor stabilized, heating was started. Once the temperature attained the steady value of 70°C, samples of the exit stream were collected. This was done for three different flow rates of the reactor feed such that the residence times were i) 25 mins., ii) 40 mins. and iii) 50 mins.

Polystyrene was precipitated from the emulsion using methanol solution. It was then dried in a dessicator and then was analysed in a gel permeation chromatograph using tetrahydrofuran as the solvent.

Limitations of the Apparatus:-

The major limitation of the set-up was the stability of flow through the reactor. The outflow could not be kept

absolutely constant for a period of time. Hence the outflow from the reactor could not be maintained equal to the inflow to the reactor.

Oxidation of the monomer could not be avoided totally, hence there were some oxidation products like aldehydes and ketones in the reactor feed.

CHAPTER 6

RESULTS AND DISCUSSION

Numerical Details: The numerical values of parameters required for the evaluation of A_4, A_5, A_7 and A_8 were taken from De Graff and Pohlein [16], Min and Ray [6] and Brandrup and Immergut [21]. A list of all such values is given in Table 1. Values of A_6 were assigned arbitrarily as 0.05 and 0.5. The cumulative particle size distribution, the total number of particles, the rate of polymerisation and the molecular weight distribution were calculated as a function of the following process variables : i) Initiator concentration, (I), ii) Surfactant concentration (S) and iii) residence time (τ). Calculations were made only for those condition as were reported by DeGraff and Pohlein 16 in their experimental study to facilitate comparison.

Numerical computations were performed on Dec-10 computer. Determination of N_T , the total number of particles, and R_p , the polymerisation rate required a minimum of about 10sec.s to a maximum of 1.2 mins. The evaluation of the moments of the molecular weight distribution, MWD, required a maximum of about 2.5 mins. of C.P.U. time.

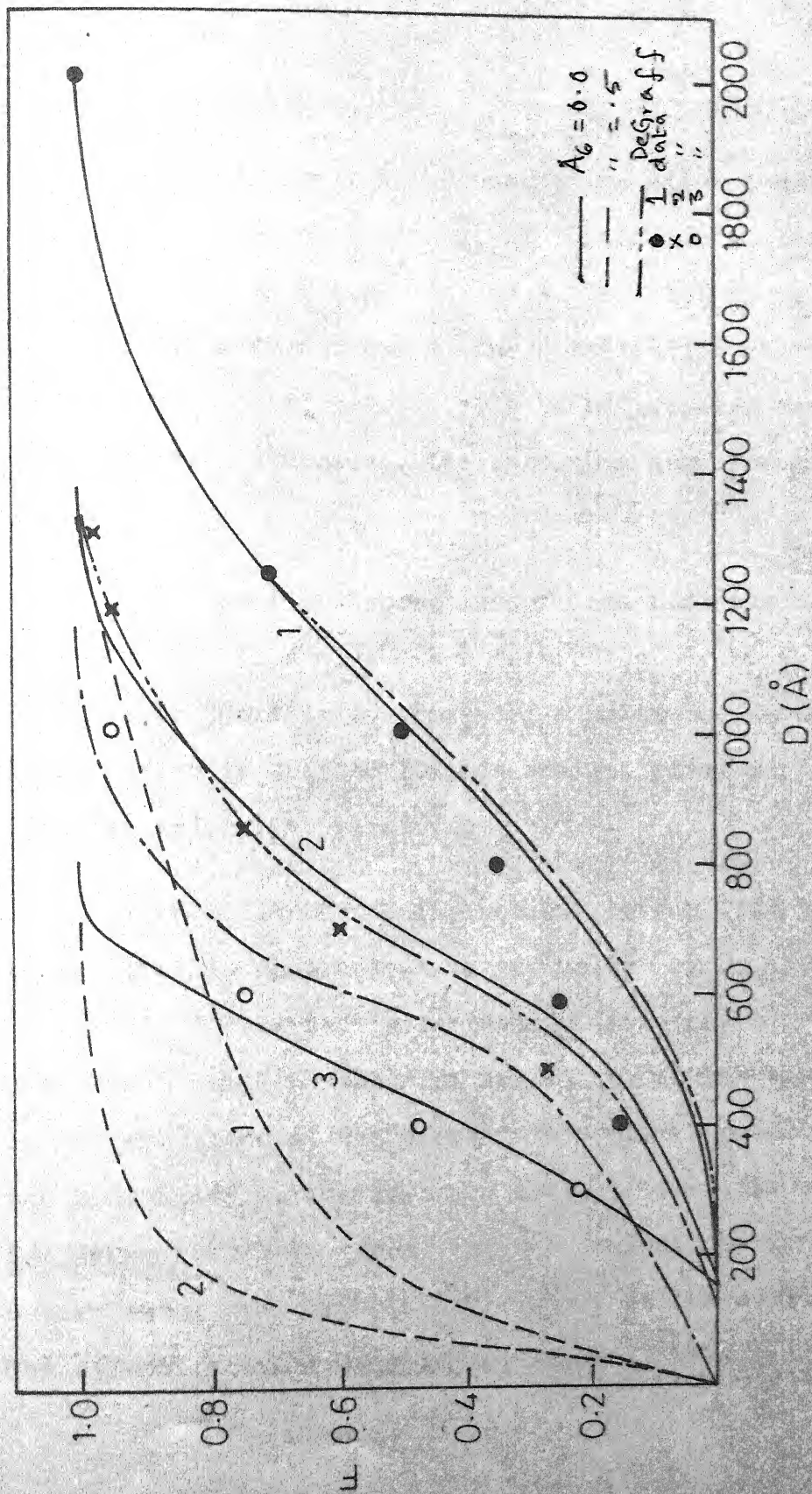


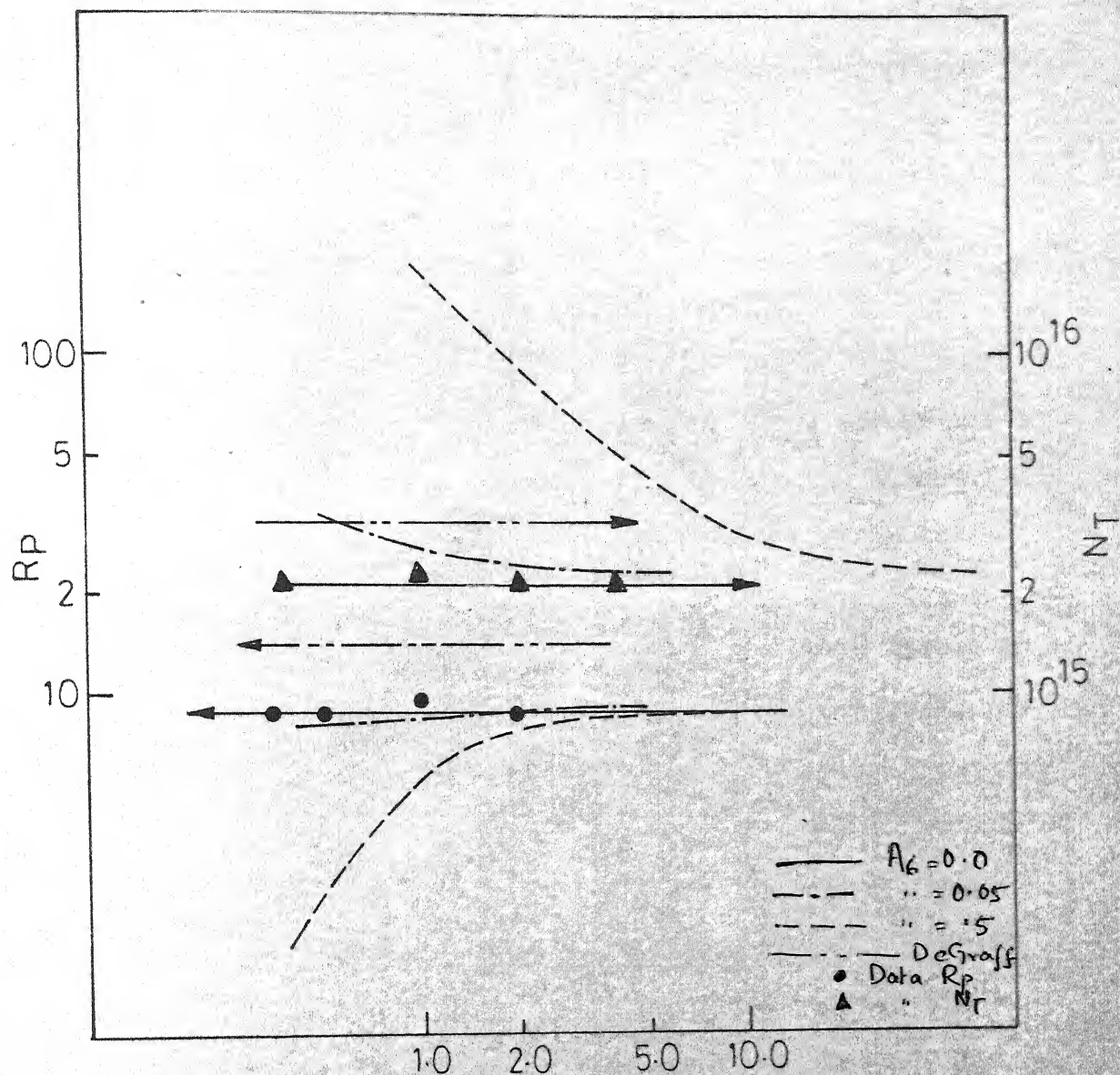
FIG.1. PARTICLE SIZE DIST. (GUM.)
1-45 MINS., 2-15 MINS., 3-7 MINS.

Particle Size Distribution

No desorption: F, the cumulative size distribution function has been plotted against particle diameter, D for different residence times in fig.1. The plot shows that as residence time is decreased, the distribution shifts towards smaller sized particles. This is to be expected since as residence time decreases, the particles grow for shorter periods.

The effect of desorption of live radicals is to decrease the particle size. When desorption occurs the effect is to lower the time of growth of a particle. Hence the distribution is shifted towards smaller sized particles. When desorption is operative.

A good fit of the theoretical curves with the experimental data is observed at larger values of D, whereas some deviation is observed in the smaller size region. The theory predicts a smaller number of smaller particles than observed in the experiments. The present theoretical prediction of the size distribution are very close to that of DeGraff's for large residence times. But the present theory shows a better match with experimental values at low residence times. The effect of desorption is not appreciable for $A_6 = .05$.



(1)
FIG. 2. N_T & R_p vs. (I)

Since the effect of desorption is to decrease the particle size, a slightly larger value of A_6 may fit the experimental data better.

N_T and R_p

Effect of Initiator Concentration: It is observed from fig.2, that as (I) goes up from about 0.3 (gm/100 gms. H_2O), both N_T and R_p remain unchanged. The constant value reached for N_T is about 2.14×10^{15} = /cc., and that for R_p is about 8.8 moles/lit,hr. It can be inferred that (I) does not affect N_T because after a certain threshold concentration of (I), the radical concentration in the reactor is fairly high in proportion to the micelles present and therefore no new particles are formed. Only the frequency of radical capture is increased. R_p too is proportional to the concentration of growing particles. Thus R_p also reaches a constant value beyond a certain value of (I). However very low (I) would decrease both N_T and R_p since then radical concentration would be very low. The theory also predicts that at zero concentration of (I) both N_T and R_p become zero, as expected.

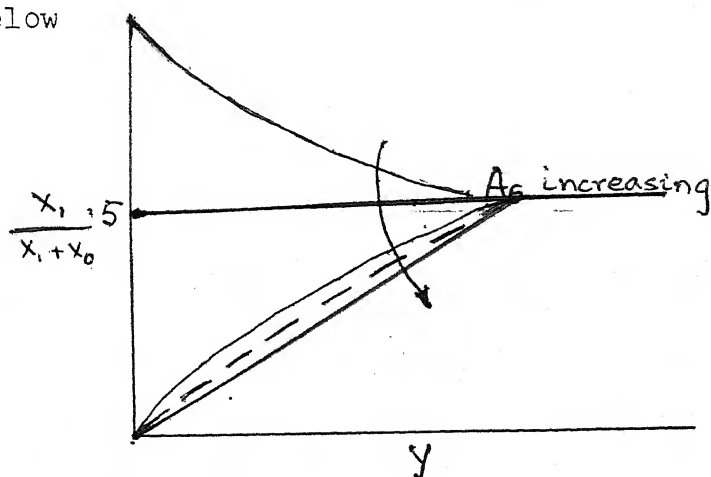
When desorption is operative the theoretical curve for N_T shows a gradual decline from a high value, till it merges with the line for no desorption. R_p shows an increase from a

low value to the constant value attained by R_p for no desorption. When (I) is large, the radical concentration is high and hence the effects of desorption become unimportant. Thus at large values of (I) the curves for no desorption and with desorption should merge. The behaviour at lower values of (I) can be explained by noting that desorption impedes the growth of polymer particles. The smaller particles require less soap for stabilisation, hence more soap is available as micelles. This causes an increase in the number of particles. But as (I) increases and more radicals are available, they begin to counter the effect of desorption by promoting growth rate. Therefore N_T starts decreasing with (I) and finally merges with the curve for no desorption.

R_p is proportional to the number of growing particles i.e. $\frac{X_1 N_T}{X_0 + X_1}$. Now from 1, $\frac{X_1}{X_0 + X_1}$ can be written as equal to

$\frac{A_5 + A_4 y^{2/3}}{A_5 + 2A_4 y^{2/3} + A_6 y^{-1/3}}$. This function has been sketched with y

below



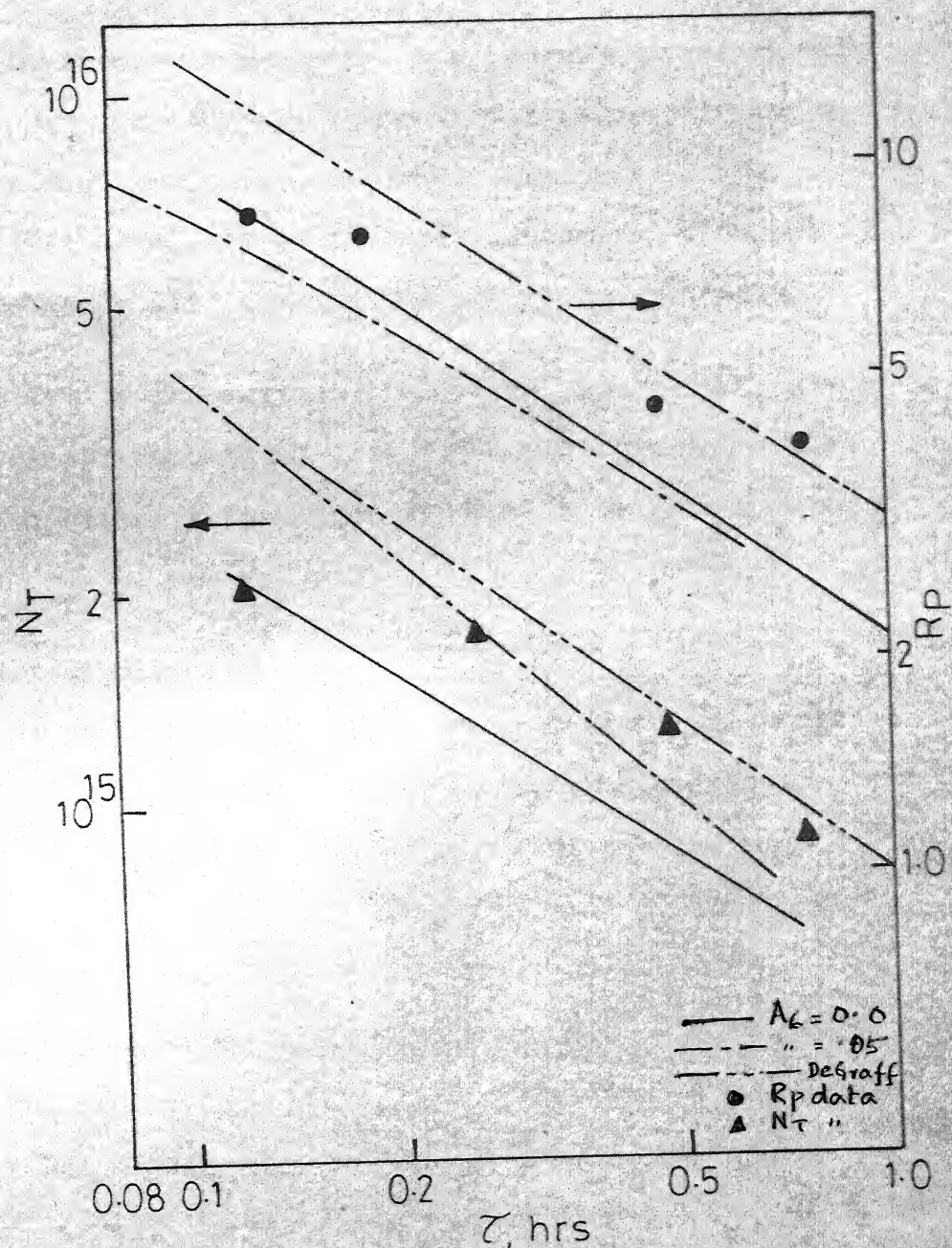


Fig. 3. N_T and R_P vs. τ

It is seen that increasing desorption causes a corresponding decrease in $\frac{X_1}{X_0 + X_1}$ for all sizes of particles. Therefore R_p decreases when desorption is present inspite of the enhanced values of N_T . It increases continuously with (I) till it begins to merge with the results for no desorption.

Good fit of theoretical predictions for no desorption with experimental results is seen. It can be concluded that desorption is either inoperative or present only to a minor extent.

Effect of Residence time: It is seen in fig.3 that both N_T and R_p fall continuously with τ . As τ is increased the particle size increases and more soap is required to stabilise them. Consequently less number of micelles are available for nucleation of particles thereby decreasing N_T . Thus N_T and R_p , which is proportional to N_T , both decrease with τ . However the theory predicts that when τ is equal to zero, both N_T and R_p would be zero. Thus both N_T and R_p must first rise to a maximum value and then begin to fall with τ . This is to be expected because at low residence times, as the residence time increases more particles would be created and hence both N_T and R_p would increase.

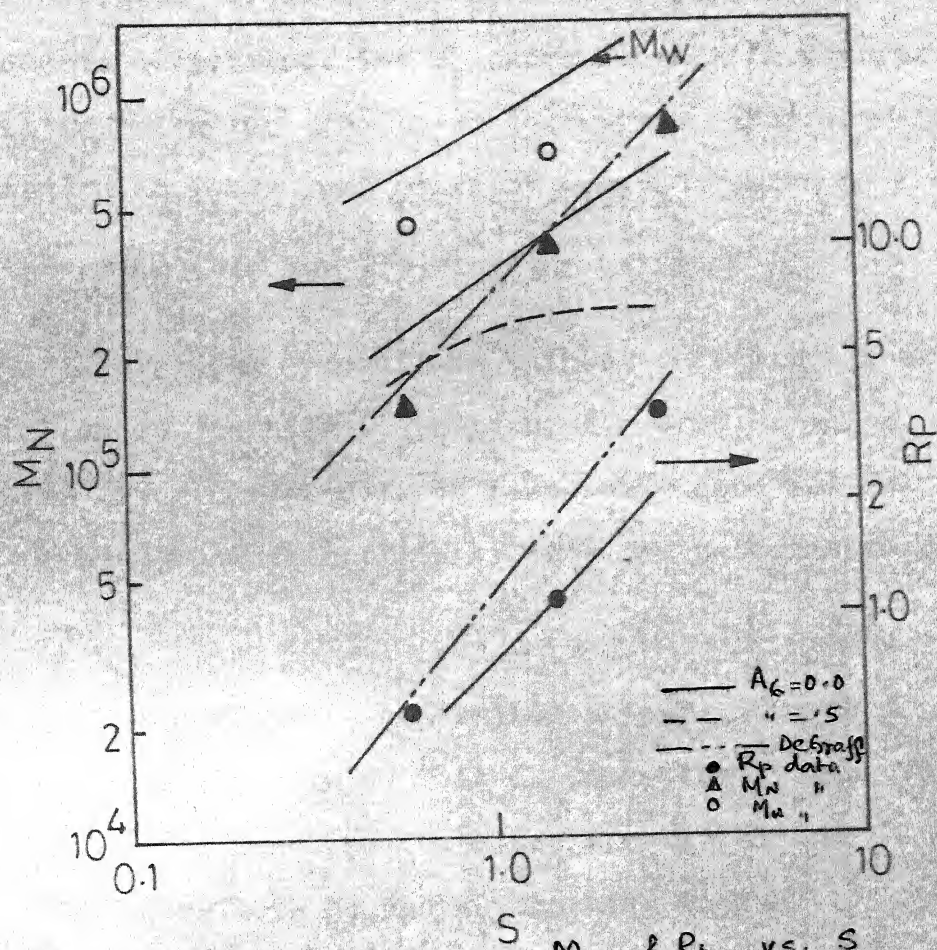


FIG. 4. M_n & R_p vs. S

As discussed earlier desorption increases the number of particles and essentially leaves R_p unaffected. Thus the nature of variation of N_T and R_p versus τ remains unchanged due to desorption. The R_p curve for finite desorption lies a little below the one for no desorption. This also is to be expected as R_p is influenced by $\frac{X_1}{X_1 + X_0}$ which as shown earlier is responsible for lowering the value of R_p .

The theoretical predictions without desorption show some deviation in the high τ region, for both N_T and R_p . The fit with experimental data is reasonably good for low residence times. Some desorption effects can be detected in the plot.

Effect of surfactant concentration: R_p is seen to rise steeply with S in fig.4. This is understandable because as more soap is fed more particles are created through micelles. Therefore both N_T and R_p increase with (S) .

A fair fit with experimental data is found and the match is no better than that of DeGraff's theory with the experimental points.

Number average molecular weight

Effect of (I) :- M_n is observed to fall steeply with (I) in

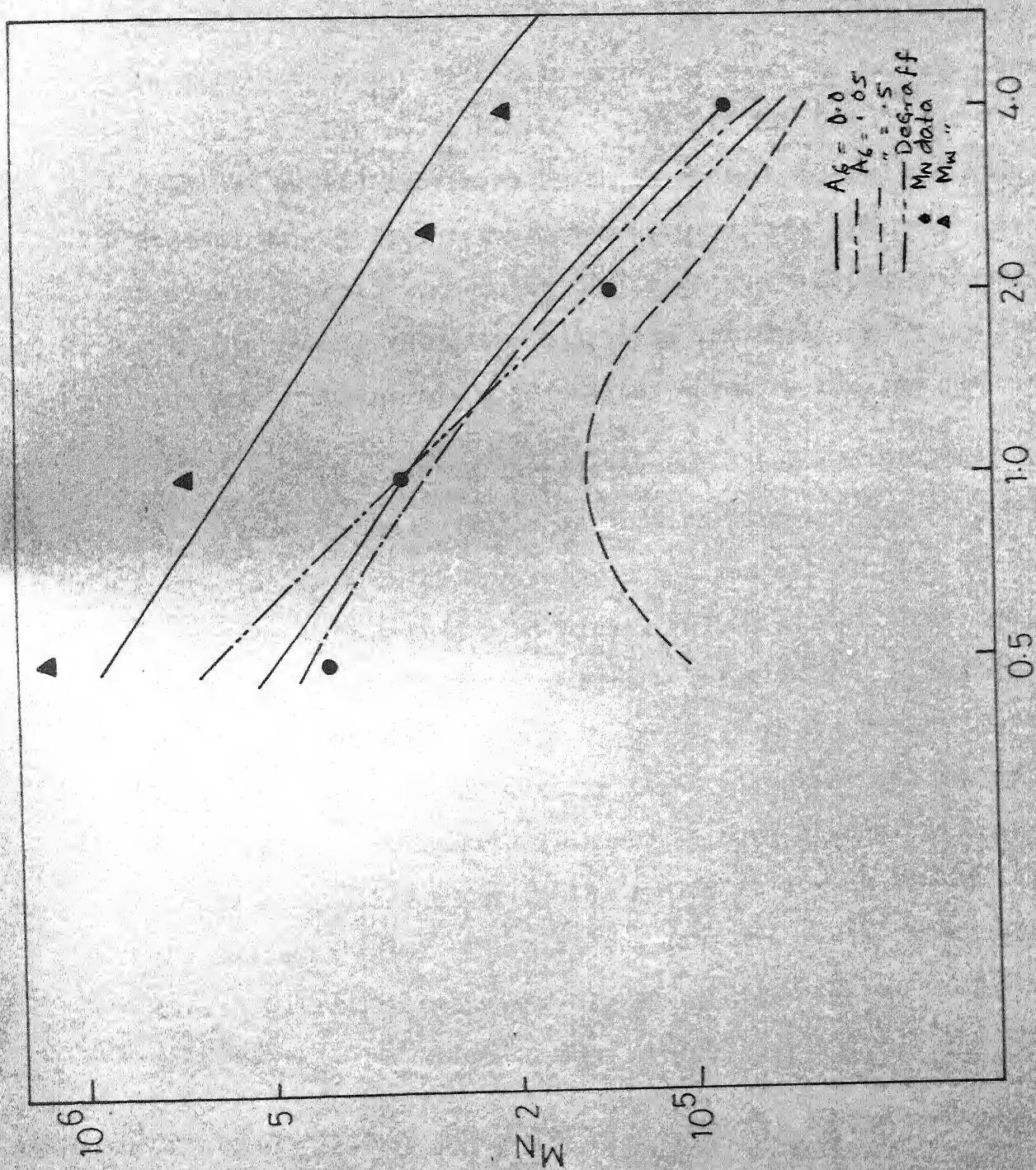


Fig. 5. M_N vs I_0

fig.5 after a certain value of (I) (around 1gm /100 gms H_2O). The rate of decrease is a little slower below this concentration. An explanation for this phenomenon is that, M_n is zero when (I) is zero but would increase with (I) for low values of (I). But as (I) increases beyond a certain value, rate of radical supply to the particles becomes high and hence live radicals created within the particles are terminated faster, with the result that time available for their growth is less. Then small chains are produced and a low M_n results.

When desorption is present the curve for A_6 equal to .05 follow the line for no desorption closely. However, the curve for $A_6 = .5$ clearly show a maximum but follows the curve for no desorption at higher values of (I). Both the lives (ie for $A_6=0.05$ and 0.5) are below in for no desorption. This can be explained by the fact that at high (I) the desorption effects are not important since radical supply is large and both curves with and without desorption should follow each other closely. Again at very low values of (I), the radicals enter the particles less frequently and desorption drastically decreases the growth time of the radicals leading to a low value of M_n .

The fit of the theoretical prediction with experimental data is reasonably good for $A_6 = 0.0$ and $A_6 = 0.05$.

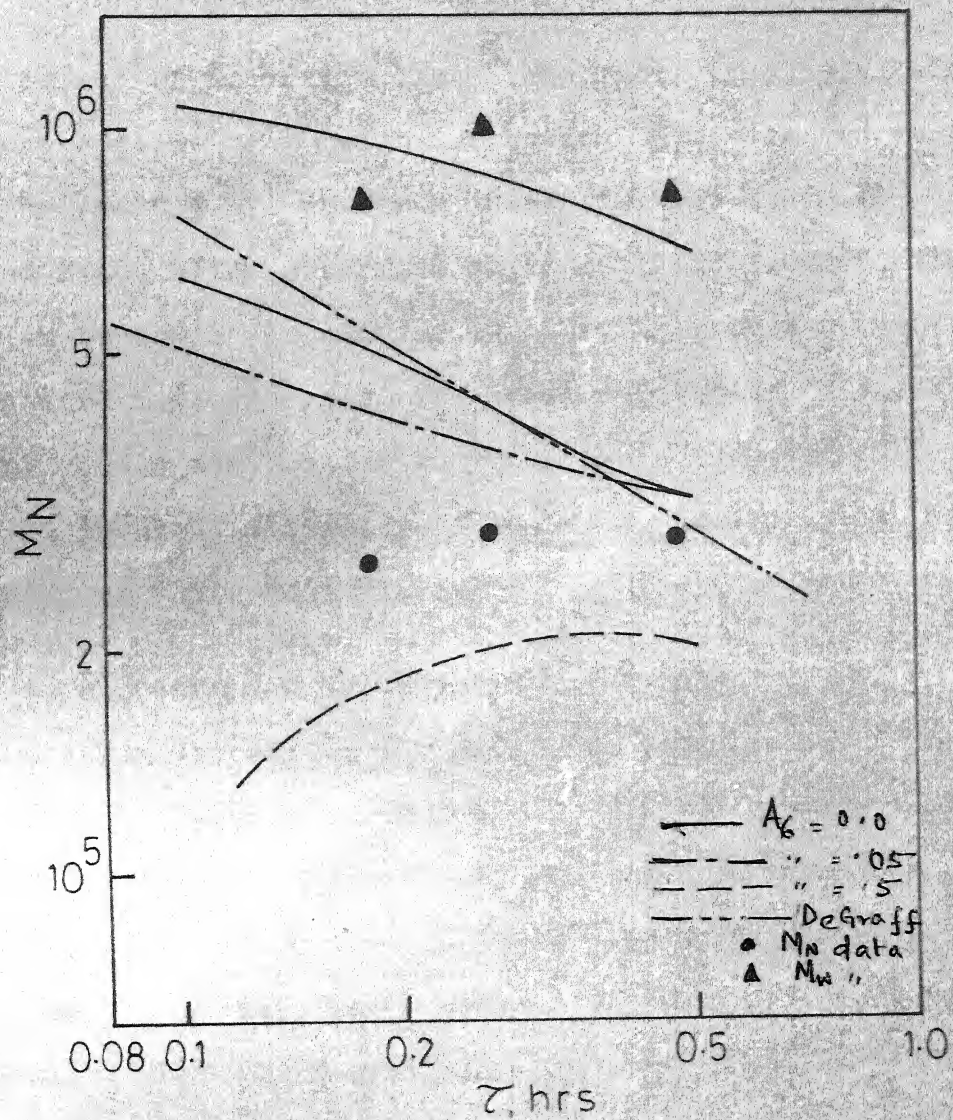


Fig. 6 M_n vs. τ

It can be inferred that desorption effects are not that important.

Effect of Residence Time: The theoretical plot shows a gradual decline of M_n with increasing τ , over the range of 0.1 hr. to 0.5 hr. as shown in fig.5. This is to be expected since after a certain value of τ is reached, the particles become large and due to their increased surface area, absorb more radicals. The increased supply of initiator radicals causes small chain to form within the particles and thus M_n is lowered. Initially of course M_n is zero when τ is zero and must rise to a maximum.

When desorption is operative, the plot depicts a maxima clearly whereafter the curve follows the curve for no desorption. Desorption causes size reduction of particles, hence the initiator supply to the particles is reduced. Therefore M_n increases with τ for a longer period than when desorption is absent. Once however, the particles have grown appreciably, they start absorbing initiator radicals faster and the same behaviour of M_n with τ is observed as with no desorption. So the effect of desorption is to shift the maxima towards higher values of τ .

Fit with the experimental data is poor, but is better than that of DeGraff's theory. The inflexion observed in the

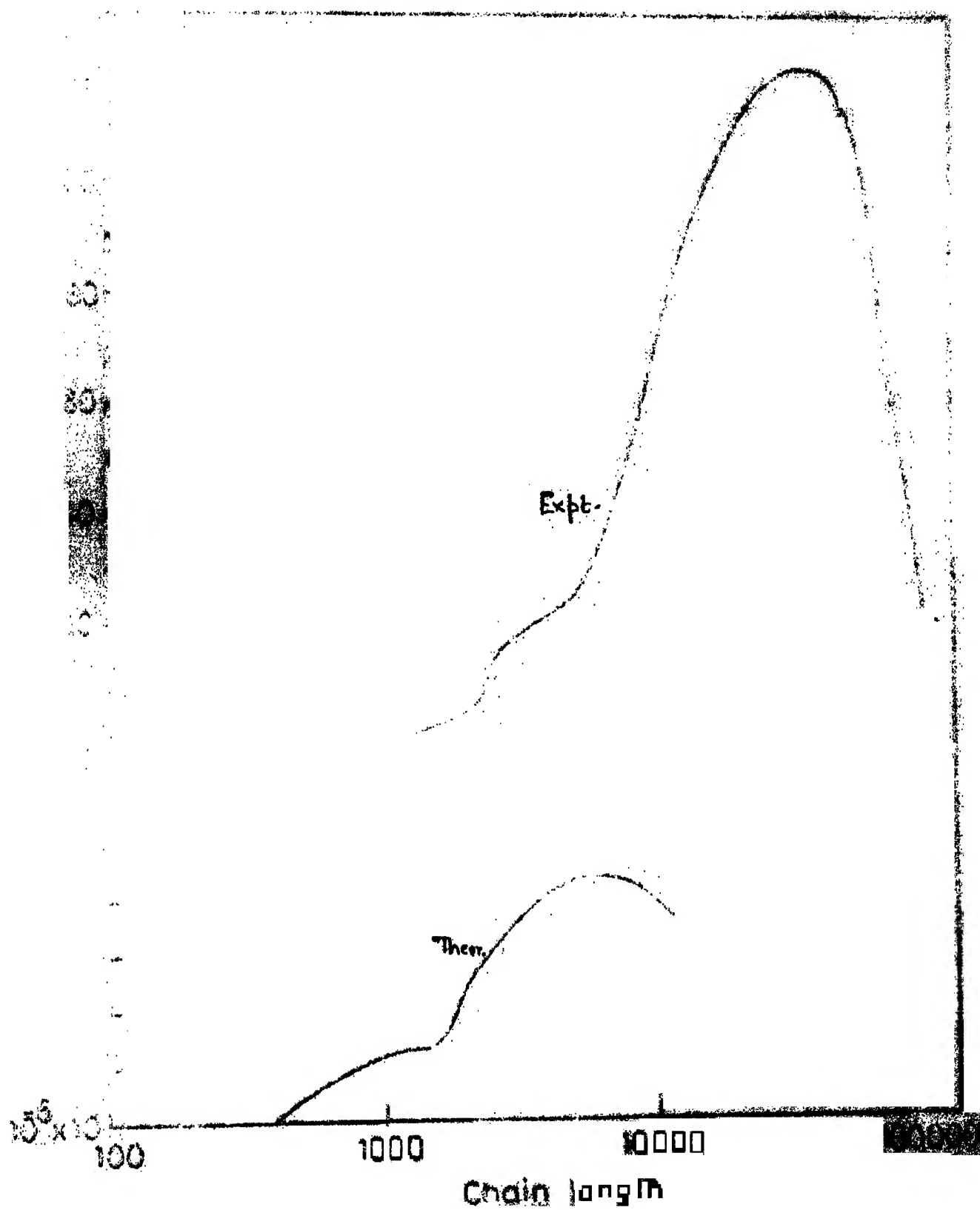


Fig. 7. M-H-D

Fit of the theoretical curve with experimental data is fair, being about as good as DeGraff's predictions.

Molecular Weight Distribution:

The experimental values obtained in the present work show a very poor fit with the theoretical prediction of M.W.D., due to the fact that the confidence in the experimental results is rather low.

CHAPTER 7CONCLUSIONS

1. The present work is an extension of the Thompson and Stevens model [12] for the calculation of number of particles, rate of polymerisation and the molecular weight distribution, alongwith the absolute particle size distribution.
2. Results obtained by using this model have been found to be similar to those of the RTD model of DeGraff. In some cases the fit of the theoretical prediction with experimental values has been found to be better than DeGraff's theoretical predictions.
3. The model could be made better by considering the re-entry of live radicals into the polymer particles.
4. Improvements in the present apparatus would be needed to obtain reliable experimental data. In particular proper flow rate control is required.

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TABLE I

| | Constant | Units | Value | Ref.No. |
|-----|----------|--|---------------------------|----------|
| 1. | K_p | $\text{cm}^3/\text{mole}, \text{sec.}$ | 2.65×10^5 | (16) |
| 2. | K_d | $1/\text{sec.}$ | 2.33×10^{-5} | (16) |
| 3. | K_{tr} | $\text{cm}^3/\text{mole}, \text{sec.}$ | 21.2 | (21) |
| 4. | d_p | gms/cm^3 | 1.0526 | (16) |
| 5. | v_m | cm^3 | 65.4498×10^{-21} | (6) |
| 6. | v_d | cm^3 | 4.1888×10^{-12} | assumed |
| 7. | a_s | cm^2/mole | 3.672×10^9 | (16) |
| 8. | M_p | moles/lit | 5.2 | (16) |
| 9. | d_m | gms/cm^3 | 0.878 | (16) |
| 10. | S | $\text{gms} / 100 \text{ gms H}_2\text{O}$ | 1 | Pr. Work |
| 11 | I | " " | .1 | " |

Appendix I

Check on the consistency of Boundary Conditions

We know that:

$$X_0 = \frac{X_1 (\Lambda_6 y^{-1/3} + \Lambda_4 y^{2/3})}{\Lambda_4 y^{2/3} + \Lambda_5}$$

$$\text{or } f(0, v) = f(1, v) \frac{(\Lambda_6 y^{-1/3} + \Lambda_4 y^{2/3})}{\Lambda_4 y^{2/3} + \Lambda_5}$$

$$\text{From (6); at } y = 1, f(1, v_m) = \frac{R_{ia} a_m N_A}{K}$$

$$\therefore f(0, v_m) = f(1, v_m) \frac{\Lambda_6 + \Lambda_4}{\Lambda_4 + \Lambda_5} \quad (Ia)$$

Next, writing a balance on $f(0, v)$ particles lying in a volume range of v_m to $v_m + \epsilon v_m$ we have:

$$0 = \underbrace{f(0, v_m + \frac{\epsilon v_m}{2})}_{\sim} \epsilon v_m + f(0, v_m + \frac{\epsilon v_m}{2}) \epsilon v_m a_p R_{ia} N_A - f(1, v_m + \frac{\epsilon v_m}{2}) \epsilon v_m (\frac{k_0 a_p}{v} + R_{ia} a_p N_A)$$

Taking limit $\epsilon v_m \rightarrow 0$ and $a_p \rightarrow a_m$ We have:-

$$f(0, v_m) = f(1, v_m) \frac{\frac{K_0 a_m}{v_m} + R_{ia} a_m N_A}{1 + R_{ia} a_m N_A}$$

$$\text{or } f(0, v_m) = f(1, v_m) \frac{\Lambda_6 + \Lambda_4}{\Lambda_5 + \Lambda_4} \quad \text{which is same as (Ia)}$$

Hence the consistency of b.c. on $f(1, v_m)$ has been verified.


```

00050 C THIS PROGRAM CALCULATES TN(TOTAL NUMBER OF PARTICLES)AND RP
00051 C (RATE OF POLYMERISATION)
00100 DIMENSION X(6),D(6),H(6),T(6),A(6),SUM(80000)
00200 Data K/800000/,T/-.90618,.,53847,0.,.53847,.,90618/
00300 Data A/.23693,.,47863,.,56888,.,47863,.,23693/
00400 TOT=0.
00500 N=1
00600 DO 50 M=500,K,500
00700 SUM(M)=0.
00800 DO 65 I=1,5
00900 X(I)=(T(I)*(M-N)+M+N)/2.
01000 H(I)=F(X(I))
01100 D(I)=H(I)/X(I)**(-1./3.)
01150 C REPLACE H BY D TO CALCULATE RP
01200 SUM(M)=SUM(M)+A(I)*H(I)*(M-N)/2.
01300 65 CONTINUE
01400 N=M
01500 TOT=TOT+SUM(M)
01600 50 CONTINUE
01700 TYPE*,(SUM(J),J=80000,K,80000)
01750 C THIS IS DONE TO TEST CONVERGENCE
01800 TYPE*,TOT
01900 a4=.0000232
02000 a5=.0000745
02100 a6=.05
02200 a3=.672*10**9
02300 s1=2.79/(154*278)
02400 a0=78.54*10.**-14.
02500 b0=3.036
02600 a1=1./(1.+a4/a5+2./3.*(a4/a5)*TOT)
02700 r0=36.*10.**5.*228.79*10.**-23.*a4*tot*a1*a0
02720 C TO EVALUATE RP DETERMINE TOT USING H IN 1200
02750 TN=A1*A4*A0/A5
02800 r0=r0*10.**17.
02900 TYPE*,TN
03000 STOP
03100 END
03200 FUNCTION F(X)
03300 G1=X**(-1./3.)
03400 G2=2.*(X-1.)
03500 A4=.0000232
03600 A5=.000037
03700 A6=.05
03800 G3=1.5*A6/A4
03900 G4=ALOG((A5/A4+X**(2./3.))/(A5/A4+1.))
04000 G5=3.*(A5/A4)*(X**(1./3.)-1.)
04100 G6=3.*(A5/A4)**(3./2.)
04200 G7=atan((A4/A5)**(1./2.))*X**(1./3.)-atan((A4/A5)**(1./2.))
04300 F=G1*EXP((-A5)*(G2+G3*G4-G5+G6*G7))
04400 RETURN
04500 END

```

```

0050 C THIS PROGRAM IS USED TO CALCULATE THE FIVE LEADING MOMENTS
0060 C OF THE MND
0100 DIMENSION A(4),B(4),P(4),Q(100),Y(100),F(100),C(4,3)
0200 DATA EPS/15.,DX/15.,N/5,TOT/207.25/
0300 C(2,1)=153.6
0400 C(2,2)=0.0
0500 C(3,1)=153.6
0600 C(3,2)=307.2
0700 C(4,1)=153.604
0800 C(4,2)=460.8
0900 C(4,3)=460.8
1000 A7=C(2,1)
1100 H=DX*.5
1200 X=1.0
1250 C INITIAL CONDITION,Y(I)=0 ATX=1
1300 DO 10 I=1,N
1400 10 Y(I)=0.0
1401 A4=.0000232
1402 A5=.0000745
1403 A6=.0123
1500 S=1./(1.+A4/A5+2.*(TOT+A4/(3.*A5)))
1550 C INITIAL CONDITION,Y'(I)=THE FOLL. ATX=I
1600 Y(6)=(A4+A5)*A4*A5/A5
1700 Y(7)=(A6+2.*A4)*A4*S/A5
1800 Y(8)=(A6+4.*A4)*A4*S/A5
1900 Y(9)=(A6+8.*A4)*A4*S/A5
2000 Y(10)=(A6+16.*A4)*A4*S/A5
2100 C GILL'S ALGORITHM
2150 DO1 I=1,10
2200 1 O(I)=0.
2300 A(I)=0.5
2400 B(I)=2.
2500 P(I)=0.5
2600 A(2)=1.-SQRT(0.5000000)
2700 B(2)=1.
2800 P(2)=A(2)
2900 A(3)=1.+SQRT(0.5000000)
3000 B(3)=1.
3100 P(3)=A(3)
3200 A(4)=1./6.
3300 B(4)=2.
3400 P(4)=.8
3500 DD3J=1,4
3600 4 CALL FUNC(X,Y,C,N,S,F)
3700 DO12I=1,10
3800 D=A(J)*(P(I)-B(J)*Q(I))
3900 H1=D*DX
4000 Y(I)=Y(I)+H1
4100 H2=D*3
4200 H3=P(J)*F(I)
4300 H2=H2-H3
4400 O(I)=O(I)+H2
4500 12 CONTINUE
4600 12 IF(J.EQ.1 .OR. J.EQ.3)X=X+H
4700
4800
4900
5000 3 CONTINUE
5100 DO50 I=1,N
5200 50 IF(ABS(Y(I+N)).GT.EPS)GO TO 60
5300 TYPE*,X,EPS,DX,(Y(IJ),IJ=1,10),(O(I),I=1,10)
5400 GO TO 70
5500 60 GO TO 4
5600 70 STOP
5700 END
5800 SUBROUTINE FUNC(X,Y,C,N,S,F)
5900 DIMENSION Y(100),F(100),C(4,3)
6000 A4=.0000232
6100 A5=.0000745
6200 A6=.05
6300 A7=153.6
6400 A8=.0123
6500 G1=A6/X**(.1/3.)+A4*X**(2./3.)
6600 G2=A4*X**(2./3.)+A5
6700 G3=2.*(X-1.)+(1.5*A6/A4)*(ALOG((A5/A4+X**(2./3.))/(A5/A4+1.)))
6800 G4=3.*(A5/A4)*(X**(.1/3.)-1.)
6900 G5=3.*(A5/A4)**1.5*(ATAN((A4/A5)**.5*X**(.1/3.))-ATAN(A4/A5)**
7000 1.5)
7100 X0=(G1/G2)*A4*S*EXP(-A5*(G3-G4+G5))
7200 FF=-(A5+A6*X**(-1./3.)+A4*X**(2./3.))+AB)
7300 X1=((A4*X**(2./3.)+A5)*X0)*X**(.1/3.)/(A6+A4*X)
7400 G=A4*X**(2./3.)*X0+A8*X1
7500 DO20 I=1,N
7600 20 F(I)=Y(I+N)
7700 T=A4/(A4*X**(2./3.)+A8)
7800 F(6)=(2.*X**(-1./3.)*T/3.+FF)*Y(6)+G*A4/(T*A5)
7900 F(7)=(2.*X**(-1./3.)*T/3.+FF)*Y(7)+Y(6)*(C(2,1)+2.*X**
8000 1(-1./3.)/3.)+G*(A4*X**(2./3.)/A5+A4/(T*A5))

```